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# OPTICAL CHANGES IN CERIUM-CONTAINING GLASS AS A RESULT OF ACCELERATED EXPOSURE TESTING

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## ABSTRACT

The purpose of this paper is to report changes in the optical transmission spectrum (solarization) of commercial low-iron cerium containing glass (CG). UV absorption by CG has been shown to reduce yellowing rates of EVA polymeric pottants in PV modules resulting from UV radiation. Absorption and fluorescence spectra of CG change with exposure to UV light in the glass matrix. Solarization of CG could cause changes in the glass transmission that may result in changes in the UV protection and the efficiency of the module. We are studying the solarization of glasses in a variety of accelerated light exposure chambers at intensities ranging from 1 to more than 1000 suns. Measurements made at various stages of the accelerated exposure tests are presented.

## INTRODUCTION

We have studied changes in the optical transmission spectrum (solarization) of commercial low-iron glass containing cerium (CG) after exposure to simulated and high-flux terrestrial solar irradiance [1]. CG has recently been used in the manufacture of photovoltaic (PV) modules because of its high visible light transmittance and for its absorption of light below about 350 nm. The spectral location of the UV absorption edge depends upon the Ce concentration in the glass. The UV absorption exhibited by Ce-doped glass has been shown to reduce yellowing rates of EVA polymeric pottants in PV modules caused by damaging UV radiation [2-4]. However, the long-term protective stability of the cerium-containing glass superstrate for EVA pottants has yet to be established. Solarization of CG could result in undesirable changes in the absorption spectrum of the glass. Protection from UV degradation of the polymer pottant could be lost if the UV absorption of the glass degrades due to solarization. Another outcome of solarization might be a decrease in the transmission properties of the glass across the solar spectrum resulting in a glass with lower transmittance, which would reduce the efficiency of the PV modules. We have begun accelerated solarization studies to determine if optical changes occur and, if so, to what extent.

Specialized glasses with specific transmission and absorption properties are produced for many applications. The need for high transmittance glass as a superstrate for PV modules is important for good performance. The reduction in the rate of yellowing of EVA is also an important property of CG. The addition of cerium to glass, especially low-iron glass, results in an exceptionally clear product, partially as a result of the intense blue fluorescence of the cerous ($Ce^{+3}$) ion. These glasses absorb high energy radiation and have been used as screens in low Earth orbit and space power applications [5,6]. During the lifetime of devices using cerium-containing glass, the absorption and fluorescence spectra of the glass changes with exposure to UV light as the cerous ion is converted to the ceric ion ($Ce^{+4}$) within the matrix of the glass. The cerous/ceric ratio of the glass is established by the furnace conditions at the time of manufacture; this ratio influences the initial transmission properties of the glass. A highly oxidizing furnace environment produces glass with almost no cerous ions, while a reducing environment yields almost none of the ceric species. To maximize visible and near infrared light transmission, commercial CG typically contains primarily the cerous ion [7,8].

Because the actual UV/VIS absorption spectra, peak positions, and intensities depend greatly upon minor constituent impurities present in the glass, the best approach for monitoring the solarization process is to measure the absorbance and fluorescence of samples of glass as a function of exposure to simulated or actual solar irradiance [9]. Because the cerous ion has an intense fluorescence spectrum and the ceric form exhibits no fluorescence, fluorescence analysis provides a convenient and highly sensitive method to monitor the change in oxidation state of the cerium as the glass solarizes. UV/VIS transmission/absorption measurements also provide data on the extent, if any, of wavelengthdependent changes in absorption that occur in the glass as a function of exposure.

## EXPERIMENTAL

Two inch square glass coupons were prepared from 1/8-inch thick PPG Solarphire® float glass containing 0.2 wt.% Ce [10]. The glass samples were exposed with several different accelerated weathering systems and also outdoors at 1 terrestrial sun in Golden, Colorado. Coupons were exposed in parallel in an Atlas Weatherometer at 1 sun, and in a XENO test chamber at approximately 2 suns. Both of these weathering chambers provide exposure to filtered Xenon arc light and are operated at 60°C and 80% relative humidity (RH).

Coupons were exposed to concentrated natural sunlight in two different configurations and at two flux levels. In the first configuration, samples were exposed to concentrated sunlight with wavelengths below 600 nm at a nominal flux of 100 suns at NRELs High Flux Solar Furnace (HFSF). Photons with longer wavelengths are not likely to affect the glass solarization process and thus were excluded. The reduction in the number of long wavelength photons results in a lower thermal load on the samples. This, coupled with an actively cooled sample stage, allows samples to be exposed for extended periods of time while maintaining the glass coupons below 110°C during the entire process. In the second exposure configuration, samples are exposed at the HFSF to highly concentrated full-spectrum solar radiation above 1000 suns. Sample temperatures were held below 100°C during these exposures. With this arrangement, samples have been exposed to a photon dose equivalent to 8 years outdoors in Golden.

Samples were periodically removed from weathering chambers and from outdoor racks for transmittance and fluorescence spectral measurements. Transmittance spectra data were collected on a Perkin-Elmer UV/VIS/NIR Lambda-9 spectrophotometer; fluorescence measurements were made with a ISAJY-SPECS S112XI spectrofluorometer.

## RESULTS AND DISCUSSION

Samples of Ce glass exposed to accelerated weathering show an obvious solarization effect. The solar-weighted hemispherical transmittance of the glass drops about 2%. Most of the loss in transmittance occurs above 800 nm and thus has little effect on the transmission of visible light. All samples exposed to concentrated photons in all chambers showed similar transmission curves. Samples exposed outdoors only one month also showed a similar 2% drop in the solar-weighted transmission. To the limit of the exposure conditions applied in this study, the solarization of this glass appears to be self limiting to about a 2% loss in the solar weighted transmission. In Fig. 1, the change in transmittance as a result of the outdoor equivalent photon dose of 8 years in Golden, CO. is shown. The Ce glass exhibits a loss in transmission from 800 nm and extending into the NIR. A red shift in the high energy cutoff position is also observed as the $Ce^{+3}$ initially present in the glass is oxidized to the $Ce^{+4}$ state, resulting in an increase in absorption in the 330 nm to 400 nm region of the UV portion of the spectrum, as shown in Fig. 2. This slight increase in optical density results in some additional UV screening potential of the glass and also gives the glass a very slight yellow color. It should be noted that this additional UV screening still does not result in the complete exclusion of damaging radiation, but simply attenuates an additional fraction of the light in this wavelength regime. This effect should provide more protection for UV-sensitive materials.

The loss of fluorescence intensity as a function of photon dose is shown in Fig. 3. The conversion of $Ce^{+3}$ to $Ce^{+4}$ is nearly complete after a photon dose equivalent to 5 years outside in Golden. The rate of change appears to slow as a function of exposure, resulting in what appears to be a self-limiting process. Thus, these preliminary ultra-accelerated tests suggest that the solarization process appears to be self-limiting, as there is little additional change in the transmittance spectra of the glass even after the equivalent of an 8 year photon dose.

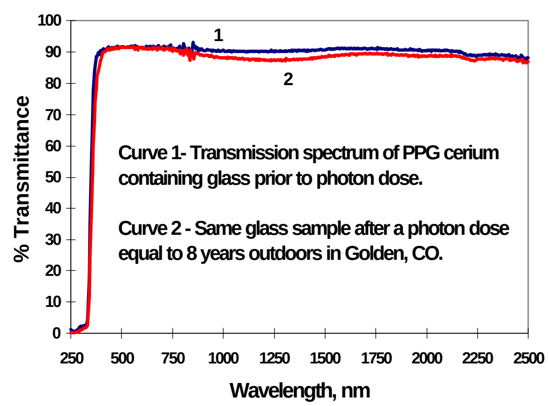


**Figure 1**. Comparison of the transmittance spectra of an unweathered Ce glass coupon and the same sample after exposure to a concentrated photon dose equivalent to 8 years outside in Golden, Colorado. The exposure results in about a 2% loss in transmission across the solar spectrum.

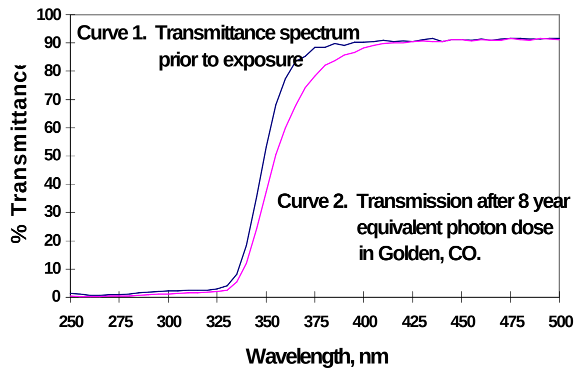


**Figure 2.** UV region of the transmission spectra of unexposed and exposed CG. Note the slight loss of transmittance from 350-400 nm. This loss results in some slight additional UV protection potential from the exposed CG.

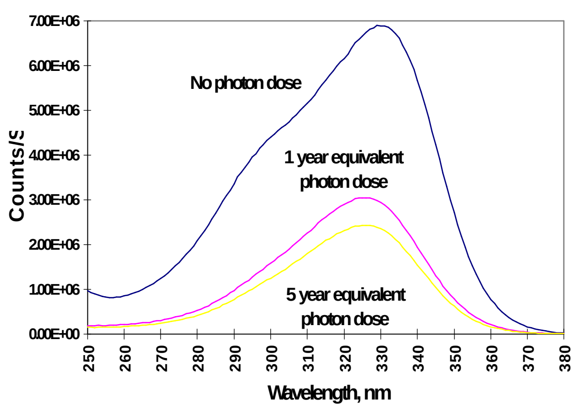


**Figure 3.** Fluorescence excitation spectra showing the loss in intensity of the emission peak at 400 nm as a result of photon dose. At the 5 year equivalent dose more than 60% of the $Ce^{+3}$ ion has been converted and the process appears to be self-limiting.

## CONCLUSIONS

PPG Cerium containing glass solarizes upon exposure to experimental weathering conditions ranging from 1 to over 1000 suns in Golden, Colorado. Samples of the exposed glass have a slight yellow edge-color and exhibit a solar-weighted decrease in transmittance of about 2%. The effect of this absorption on PV module performance will result in a decreased module efficiency that depends on the PV material used, design, etc. The additional absorption in the UV portion of the solarized glass means that the glass has some additional UV screening ability. Because the glass does not completely exclude UV photons it can extend the lifetime of materials susceptible to harmful UV radiation, but not eliminate UV-induced photothermal degradation. Solarization of CG appears to be self-limiting based on the data taken. After the initial changes, the rate of additional change slows as several years of outdoor equivalent exposure is reached.

We plan to continue this work and extend solarization studies to other glasses and to other manufacturers. It is especially critical to determine if the solarization process is self-limiting in other Ce glass formulations. The exact nature of the changes in optical properties is also important because they depend on minor trace impurities in the glass.

## ACKNOWLEDGMENTS


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